PB88-106364

New Approaches to the Decontamination of Hazardous Wastes

(U.S.) Environmental Protection Agency
Cincinnati, OH

Sep 87

U.S. Department of Commerce
National Technical Information Service
NTIS

PB88-106364

EPA/600/D-87/299
September 1987

NEW APPROACHES TO THE DECONTAMINATION OF HAZARDOUS WASTES

by

Albert J. Klee
Alternative Technologies Division
Hazardous Waste Engineering Research Laboratory
U. S. Environmental Protection Agency
Cincinnati, Ohio 45268

HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

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U.S. DEPARTMENT OF COMMERCE
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SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA *(Please read Instructions on the reverse before completing)*		
1. REPORT NO. EPA/600/D-87/299	2.	3. RECIPIENT'S ACCESSION NO. PB88-106364/AS
4. TITLE AND SUBTITLE NEW APPROACHES TO THE DECONTAMINATION OF HAZARDOUS WASTES		5. REPORT DATE September 1987 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Albert J. Klee		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Alternative Technologies Division Hazardous Waste Engineering Research Laboratory U. S. Environmental Protection Agency Cincinnati, OH 45268		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Hazardous Waste Engineering Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/12
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

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Using a chemical reagent based upon the reaction of an alkaline metal hydroxide and a polyethylene glycol, over 17,000 gallons of industrial wastes, containing chlorinated dioxins and dibenzofurans at concentrations varying from 400 to 84,000 ppm, were decontaminated to below detection levels (1 ppb in the case of the tetra-dioxins). Bioassay tests have shown that the byproducts produced from the reaction do not bioaccumulate or bioconcentrate, they do not cause mutagenicity, nor are they toxic to aquatic organisms or mammals. The equipment used for these tests is now being modified for use on contaminated soils.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED 20. SECURITY CLASS *(This page)* UNCLASSIFIED	21. NO. OF PAGES 12 22. PRICE

EPA Form 2220-1 (9-73)

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ALBERT J. KLEE
Hazardous Waste Engineering Research Laboratory, United States Environmental Protection Agency, Cincinnati, Ohio, USA

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The Hazardous Waste Engineering Research Laboratory is currently supporting a number of research projects to develop innovative chemical and biological systems capable of detoxifying hazardous wastes. Recent emphasis has been on the destruction of chlorinated dioxins, chlorinated dibenzofurans, polychlorinated biphenyls, and related organic compounds in waste liquids and in polluted soils.

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INTRODUCTION

Public concern has been growing in the United States over the use of land-based containment technologies to mitigate the problems caused by releases of hazardous substances into the environment. In response, the Office of Research and Development of the USEPA has established a formal program to accelerate the development, demonstration, and use of new or innovative technologies for dealing with hazardous waste problems. Such technologies have been termed "alternative technologies" and are defined as any unit operation or series of unit operations that permanently alters the composition of hazardous waste through chemical, biological, or physical means so as to significantly reduce toxicity, mobility, and/or volume of the hazardous waste or contaminated materials being treated.

There are three classes of alternative technologies: (1) Available Alternative Technologies, i.e., those that are fully proven and in routine commercial or private use; (2) Innovative Alternative Technologies, i.e., fully developed technologies for which cost or performance information is incomplete; and (3) Emerging Alternative Technologies, i.e., those technologies in an earlier stage of development and which have not yet successfully passed laboratory or pilot

scale testing. This paper will discuss one example, taken from chemistry, of new or emerging technology currently being sponsored by USEPA.

Physical, chemical, and biological treatment comprise a set of technology tools that can be used to prevent the release of hazardous materials into the environment or alter their nature so that they are no longer an environmental problem. For example, chemical methods can be used to reclaim diesel fuel contaminated with chlorinated dioxins. Not only does chemical treatment remove dioxins from being discharged into the environment, natural and often scarce resources may be conserved and recycled as well. Chemicals have the ability to alter the nature of materials and this fact accounts for the wide applicability that chemical treatment has in the area of hazardous waste destruction. Glycol-based reagents, for example, remove chlorine atoms from chlorinated aromatics and convert them to non-toxic glycolates.

APEG TREATMENT OF DIOXIN-CONTAMINATED MATERIALS

The APEG process

Potassium hydroxide is reacted with polyethylene glycol (of about molecular weight 400) to form an alkoxide (equation 1 below). The alkoxide reacts with one of the chlorine atoms on the chlorinated molecule to produce an ether and the potassium chloride (as shown in equation 2 below). In some APEG formulations, DMSO (dimethysulfoxide) is added to enhance the pollutant-extracting capabilities of the reagent.

Experiences with dioxin-contaminated wood preserving wastes

In February 1986, Montana Pole, a wood preserving site near Butte, Montana, contained approximately 9,000 gallons of light petroleum oil (collected previously from ground water) contaminated with chlorinated dioxins (CDDs) and chlorinated dibenzofurans (CDFs). The oil contained 3.0% pentachlorophenol and CDD/CDF homologs ranging from 422 ppb of tetra isomers to 83,923 ppb of octa isomers. Because of the presence of these dioxins and furans, the oil could

PROCESS CHEMISTRY

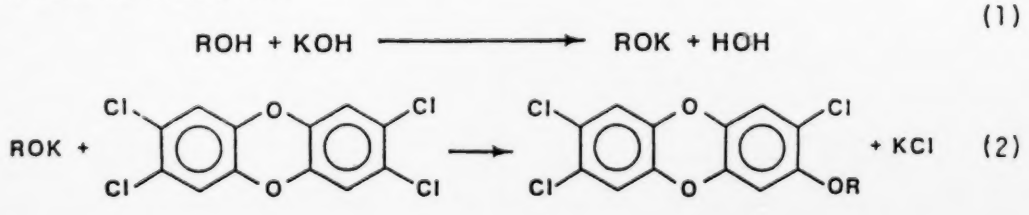

Fig. 1. APEG formulation and reactions.

not be transported off-site for incineration. The estimated cost of bringing in and operating an incinerator on-site was three million dollars.

It was decided that the APEG process would be used to decontaminate the oil. Oil samples were obtained from the site and analyzed to see whether the APEG reagent could decontaminate the oil, and, if so, to determine the treatment parameters necessary to effect the decontamination. Table 1 shows that the oil was decontaminated by the APEG reagent in the laboratory at conditions as mild as 70°C after 15 minutes.

As a result of these tests, in April of 1986 the USEPA proceeded to treat the contaminated oil by the APEG process. The decontamination was completed on July 20, 1986. The field equipment used to implement the APEG chemical process consisted of a 2700-gallon reactor mounted on a 45 foot trailer equipped with a boiler/cooling system and a laboratory/control room area.

Heating of the oil/reagent mixture is achieved by recirculating the oil and reagent through a recirculating pump, a high shear mixer (to provide good contact) and a tube-and-shell heat exchanger. The heat transfer fluid on the shell side of the heat exchanger is heated using a boiler or cooled through a series of radiator type air coolers. (See Figure 2.)

The oil was treated in five batches, each batch consisting of 1400 to 2000 gallons of oil and 600 gallons of APEG reagent. The mixture was heated to 150°C and allowed to react for one and one half hours before cooling. These reaction conditions were in excess of that shown to be necessary in the laboratory tests but were considered a "safety measure" in light of the newness of the process. The treated oil was pumped out of the reactor and into a tank to be analyzed to confirm that the CDDs/CDFs had been destroyed. The data in

TABLE 1.
Laboratory tests (in ppb) on Butte, Montana, samples
(The designation "ND" indicates "None Detected" in excess of the minimum detectable concentration which is listed directly below the ND designation)

	2378 tetra TCDD	Total Tetra CDDs	Total Penta CDDs	Total Hexa CDDs	Total Hepta CDDs	Total Octa CDDs
Raw Oil	28.2	422	822	2982	20671	83923
APEG Reagent at 70 °C, 15 min.	ND (0.762)	ND (0.456)	ND (1.01)	ND (1.83)	ND	ND
APEG Reagent at 100 °C, 15 min.	ND (0.858)	ND (1.25)	ND (2.09)	ND (3.36)	ND	ND

Table 2 indicates that all CDDs and CDFs were destroyed to concentrations below detection limits (generally less than 1 ppb and, in the case of TCDD, always below 1 ppb).

The APEG process successfully demonstrated that CDDs and CDFs can be destroyed in liquid wastes. The process cost in the Butte, Montana decontamination was less than 10% of the projected incineration costs. The CDD/CDF-free diesel fuel that was obtained will be sold to a dealer, further reducing the cost of the process.

Experiences with dioxin-contaminated pesticide wastes

The next site considered was a former hazardous waste processing facility located in Kent, Washington, and the waste in question contained 2,3,7,8-TCDD (dioxin) in a mixture of solvents, oil, and water. This dioxin-laden material was shipped some years ago from a pesticide manufacturer, and was the only waste remaining from a surface cleanup of the site conducted in 1984.

The cleanup contractor, was unable to find a commercial incinerator that would accept these dioxin-contaminated wastes. Three incinerators with federal permits refused to take the waste, citing (1) the lack of final federal regulations regarding burning dioxins, and (2) concern about public reaction. Regarding the latter, Greenpeace, an environmental public interest group, had opposed incineration of these wastes on a variety of technical grounds. On the basis of these observations and the problems cited above with other proposed solutions, coupled with the success that USEPA had experienced at the Butte, Montana wood preserving site, the decision was made to treat these wastes via the APEG process.

The waste material, a total of 7,550 gallons, was moved from approximately 100 55-gallon drums into a 12,000-gallon storage tank. This material, unlike

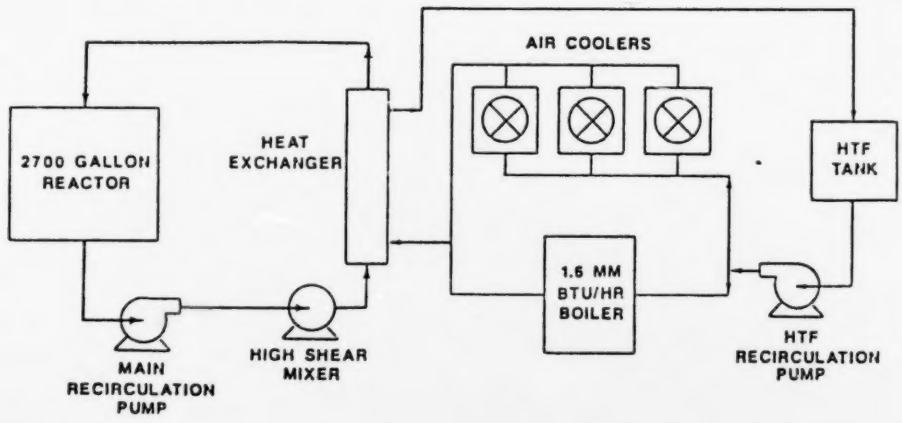

Fig. 2. Schematic of equipment for APEG process.

TABLE 2

Analyses of Butte, Montana oil after APEG treatment

(The designation "ND" indicates "None Detected" in excess of the minimum detectable concentration which is listed directly after the ND designation)

CDD/CDF	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Reagent sludge
TCDD	ND(0.64)	ND(0.68)	ND(0.82)	ND(0.75)	ND(0.80)	ND(0.12)
PeCDD	ND(0.97)	ND(0.49)	ND(0.78)	ND(0.52)	ND(0.74)	ND(1.00)
HxCDD	ND(0.92)	ND(0.63)	ND(0.43)	ND(0.70)	ND(0.90)	ND(0.44)
HpCDD	ND(0.41)	ND(0.52)	ND(0.32)	ND(0.39)	ND(0.47)	ND(0.18)
OCDD	ND(1.30)	ND(0.87)	ND(1.10)	ND(0.54)	ND(1.10)	ND(1.00)
TCDF	ND(0.77)	ND(0.59)	ND(0.83)	ND(0.62)	ND(1.50)	ND(0.14)
PeCDF	ND(1.30)	ND(0.58)	ND(0.66)	ND(0.67)	ND(1.10)	ND(0.51)
HxCDF	ND(0.84)	ND(0.53)	ND(2.20)	ND(0.67)	ND(2.10)	ND(0.49)
HpCDF	ND(0.45)	ND(1.00)	ND(1.60)	ND(0.56)	ND(1.80)	ND(0.28)
OCDF	ND(0.53)	ND(1.30)	ND(1.10)	ND(0.61)	ND(0.83)	ND(0.22)

that at the Butte, Montana site, was a very heterogeneous mixture of oils (42% by weight), solids (10 to 50%), water (28% by Karl Fischer analysis), phosphate esters (6%), pesticides, and chlorides (20,700 mg/l). The only dioxin present was 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD), at a level of 120 ppb. Although the high water content was at variance with the reported BTU content of 9,660 BTU/lb (there are a number of compounds that interfere with the Karl Fischer method), nevertheless, compared to the Butte, Montana oils, this was a very wet feed for the APEG process.

A pair of 250g samples of WP waste were decontaminated in the laboratory using the APEG process. The decontamination runs used either 25g of KOH (the standard reagent formulation) or 50g, in combination with 25g of polyethylene glycol 400 and 25g of dimethyl sulfoxide per 250g of waste oil. The data from both runs fell on the same first-order reaction curve, so the combined results, expressed as ppb dioxin remaining after a given number of hours at 115°C, are shown below:

Time, hours	Dioxin, ppb
0	120
5.5	5.5
6.5	2.5
12	<0.3

Foaming of the reaction mixture, possibly due to the presence of water and/or the phosphate esters, was observed during these laboratory trials. Reaction times required for this oil were much longer than for the Butte, Montana oil, although the total amount of chloride was similar (2-3% by weight). This was due to the (1) increased water content, and (2) lower processing temperature of

the WP material (the processing temperature at Butte, Montana was 150°C).

A total of nine processing runs (each run involved a batch of approximately 1,300 gallons of oil) were made at the site, with the results summarized below.

Final results of APEG processing of Kent, Washington wastes.
Conditions: Reaction time, 12 hours per run; temperature, 115°C.
The limit of detection for these samples as 0.3 ppb.)

Run #	Description of Waste	Final TCDD Level, ppb
1	Oil from bulk tank	<0.3
2	Oil from bulk tank	<0.3
3	Oil from bulk tank	7.1
4	Oil from bulk tank	<0.3
5	Oil from bulk tank	7.7
6	Oil & rinsate from bulk tank	<0.3
3B	Retreatment of Run 3	2.6
3C	Retreatment of Run 3B	<0.3
5B	Retreatment of Run 5	<0.3

As can be seen from this table, all of the TCDD was decontaminated to the detection level of <0.3 ppb. This level was below that required by Federal regulations for this waste material (which was <1 ppb). Foaming is the reason attributed to the failure of runs 3 and 5. Full agitation was applied in Run 3B, so this retreatment was a failure, also. However, Runs 3C and 5B were done with minimal agitation to avoid foaming, and these runs were successful in reducing the TCDD levels to <0.3 ppb. The table does not indicate, however, that the material from the earlier runs was treated several times before it was discovered that foaming was causing the contaminated oil to move out of the reactive zone in the batch reactor. Thus, although the cost of the APEG process to decontaminate the Kent, Washington waste approached $600,000 (about three times the cost of the Butte, Montana treatment), the actual number of gallons treated plus those retreated was roughly three times the quantity treated in Butte, Montana. Thus, the treatment cost per gallon for both Butte and Kent works out to about $24/gallon, i.e., 10% of the incineration costs estimated for the Butte, Montana waste.

The APEG process now has successfully destroyed chlorinated dioxins and other chlorinated pollutants from sites in both Butte, Montana and Kent, Washington. In the case of the Kent, Washington wastes, the complex nature of the material (including high moisture and solids contents), coupled with components that caused mechanical foaming problems that made treatment more difficult from an engineering point of view, the APEG process has been demonstrated to be viable even under the most difficult of circumstances.

Bicassay tests on APEG byproducts

In a chemical reaction that involves other than the very simplest of compounds, a large number of byproducts may be formed. Thus, a great deal of painstaking analytical chemistry may be involved before the complete byproduct picture is known. This is expensive and time-consuming. However, because the major goal of these APEG reagents is to convert materials that are harmful to living organisms to materials that are harmless, an effective solution is to conduct bioassay tests, i.e., tests that determine the effect of APEG byproducts on living organisms. Such tests include: (a) mutagenicity assays (such as the Salmonella or Ames test), which determines whether the byproducts cause cell mutations, (b) toxicity studies, which determine whether the byproducts cause any immediate harm (including death) to organisms, and (c) bioaccumulation tests, which determine whether the byproducts are taken up in the tissues of organisms. Related to the last-named are bioconcentration tests, which determine whether an organism concentrates the byproducts in the tissues of organisms.

The following table summarizes the results of subjecting fathead minnows to tetrachlorobenzene (TCB), and TCB reacted with an APEG reagent (TCB/APEG). Each sample noted in Table 3 consisted of 5 minnows, ground and composited to form the sample. Table 3 indicates that there is no appreciable bioaccumulation or bioconcentration of the TCB/APEG reaction byproducts in the fathead minnow.

The mutagenic activity of a compound is measured by the Ames test, which involves mixing the cells of the bacterium, Salmonella typhimurium, with the compound in question, incubating at a standard temperature, and then counting the increase in the number of colonies produced after a given period of time. Two strains of Salmonella typhimurium are commonly used, strain TA98 and strain TA100. For the evaluation of mutagens requiring metabolic activation, an extract from rat liver (called "S9") is added to the mixture. The results are considered positive (i.e., the material is mutagenic) if the increase in the number of colonies is at least double or triple that of the control.

TABLE 3

Bioaccumulation in the fathead minnow of TCB and TCB/APEG reaction byproducts

Sample	TCB in Fish Tissues, mg/g	Bioconcentration Factor	Number of Samples
Control	<0.1	0	2
0.5 ppm TCB	1735	6195	2
0.5 ppm TCB/APEG	<0.1 to 0.3	0	4

There are two versions of the Ames test: the standard Ames test and a modification developed by Dr. Norman Kado at Harvard University. The latter is generally about 10 times more sensitive than the standard assay. Table 4 shows the results of subjecting (a) the byproducts of the reaction between 2,3,7,8-tetrachlorodibenzo-p-dioxin and APEG (TCDD/APEG), (b) a pure APEG reagent, (c) DSMO, and (d) two chemicals known to be mutagenic (anthramine and 2-nitrofluorene) to the more sensitive Kado test. As can be seen from Table 4, neither the APEG-dioxin byproducts nor the APEG or DSMO itself were mutagenic.

Studies have shown that 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) is extremely toxic to fish, producing mortality in carp (Cyprinus carpio) at water concentrations as low as 60 ppq (parts per quadrillion). It is also known that carp are approximately as sensitive to TCDD as the guinea pig, the most sensitive mammalian species, and thus are a good test species to use in studies involving TCDD toxicity to aquatic organisms.

Carp (15 individuals) were exposed to a water concentration of 250 ppq of APEG/TCDD byproducts for 30 days. Conditions in a control aquarium were identical except that APEG reagent alone was injected into the water to produce a concentration equivalent to the reagent concentration in the APEG/TCDD reactant exposure aquarium. At the end of the exposure period, no fish died in either aquarium and none showed signs of TCDD toxicity. There is no evidence, therefore, that APEG byproducts are toxic to aquatic organisms.

The LD-50 (i.e., the dose required to kill 50% of a group of animals) is 0.6 ug/kg of body weight for the male guinea pig, the most sensitive mammal known. Although the LD-50 for TCDD is not known for humans, one study showed that humans exposed to 107 ug/kg developed temporary acne, but that no other symptoms were noted. Thus, the guinea pig is a highly sensitive organism in which to monitor the effects of TCDD.

TABLE 4

Mutagenicity tests (Ames test) on APEG byproducts

(Expressed as the ratio of colony counts of the test material to colony counts of the control)

	Strain TA98		Strain 100	
Material	S9	No S9	S9	No S9
TCDD/APEG	1.3	1.2	1.0	1.1
APEG	1.1	0.7	1.1	1.0
DSMO	1.2	0.7	1.0	1.0
Anthramine	41.6	-	6.1	-
2-nitrofluorene	-	14.9	-	-

Toxicity studies were conducted on male guinea pigs (36 individuals) in which 0.5, 1, 2 and 100 times the LD-50 amount of APEG/TCDD byproducts were administered orally. Similar studies were conducted using a pure APEG reagent alone. After 50 days (this time period was chosen because TCDD sometimes shows delayed toxicity that may not appear for several weeks after administration), no animals had died. In addition, weight gain and liver weight were normal. The concentrations of various liver enzymes and other components in the blood were measured, as were the levels of cholesterol, triglycerides, albumin, and total bilirubin. Elevated levels of these enzymes and other components would indicate liver damage, which is one of the toxic effects of TCDD. No increases in these enzymes and components in the blood were observed.

These bioassays indicate that the byproducts produced between APEG reagents and the pollutants studied (including TCDD) do not bioaccumulate or bioconcentrate, they do not cause mutagenicity, nor are they toxic to aquatic organisms or mammals.

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